

WHAT IS CLAIMED IS:

- 1 1. A method for fabricating a liquid containing intermixed nanoparticulate elements of
2 groups IB and IIIA and optionally VIA, comprising the steps of:
3 forming elemental non-oxide metal nanoparticles containing elements from group IB; and
4 forming elemental non-oxide metal nanoparticles from group IIIA; and
5 optionally forming elemental non-oxide nanoparticles from group VIA;
6 intermixing the elemental non-oxide nanoparticles from groups IB and IIIA; and
7 optionally VIA, wherein the particles are in a desired particle size range of between about
8 0.1 nm and about 500 nm in diameter, wherein, for each element metal, a majority of the
9 mass of the elemental metal nanoparticles range in size from no more than about 40%
10 above or below an average particle size, or, if the average particle size is less than about 5
11 nanometers, from no more than about 2 nanometers above or below the average particle
12 size; and
13 mixing the particles to form a liquid that serves as an ink.
- 1 2. The method of claim 1 wherein the group IB element is copper (Cu), the group IIIA
2 element is indium and optionally includes gallium) and the group VIA element is
3 selenium (Se) or sulfur (S) and a stoichiometric ratio of the Cu, In and Se or S in the
4 liquid is approximately $\text{CuIn}_{1-x}\text{Ga}_x(\text{S or Se})_2$, where x is between 0 and 1.
- 1 3. The method of claim 1 further comprising coating the elemental non-oxide metal
2 nanoparticles with a surfactant or polymer.
- 1 4. The method of claim 1 wherein forming the elemental non-oxide metal nanoparticles
2 includes condensing a metal vapor.
- 1 5. The method of claim 4 wherein the metal vapor includes Cu and/or In, and optionally Se.
- 1 6. The method of claim 3 wherein forming the elemental non-oxide metal nanoparticles
2 includes laser ablation, mechanical milling, grinding, nucleation from vapor, exploding
3 wires by electrical current surge, thermal decomposition of organometallic compounds,
4 sonolysis, pulse radiolysis, electrochemical reduction or chemical reduction.
- 1 7. The method of claim 1 wherein the liquid is formed by mixture with water.
- 2 8. The method of claim 1 wherein the liquid is formed by mixture with organic solvent.

- 3 9. The method of claim 1, further comprising adding a capping agent to the elemental
4 nanoparticles, wherein the capping agent selected from the group of phosphines, amines,
5 alcohols, thiols, ethers, water and glycols, trioctylphosphine oxide, trioctylphosphine,
6 triphenylphosphine, pyridine, methanol, ethanol, propanol, butanol, ethane thiol,
7 tetrahydrofuran, ethers, ammonia, methyl amine, ethylamine, ethylenediamine, and
8 acetonitrile.
- 9 10. The method of claim 1, further comprising adding a binder to the elemental nanoparticles.
- 1 11. The method of claim 1, further comprising adding a fluxing agent to the elemental
2 nanoparticles.
- 1 12. The method of claim 1, further comprising adding one or more surfactants, polymers,
2 dispersants, binders, modifiers, detergents or additives to the elemental nanoparticles.
- 1 13. A method for fabricating a liquid containing intermixed elements of groups IB and IIIA,
2 and optionally VIA, comprising the steps of:
3 forming non-oxide quantum nanoparticles containing elements from group IB; and
4 forming non-oxide quantum nanoparticles containing elements from group IIIA; and
5 optionally forming non-oxide quantum nanoparticles containing elements from group
6 VIA;
7 intermixing the non-oxide quantum nanoparticles from groups IB and IIIA and optionally
8 VIA wherein the non-oxide quantum nanoparticles are in a desired particle size range of
9 between about 0.1 nm and about 10 nm in diameter, wherein, for each element, a majority
10 of the mass of the non-oxide quantum nanoparticles range in size from no more than
11 about 40% above or below an average particle size, or, if the average particle size is less
12 than about 5 nanometers, from no more than about 2 nanometers above or below the
13 average particle size ; and
14 mixing the non-oxide nanoparticles to form a liquid that serves as an ink.
- 15 14. The method of claim 13 wherein the non-oxide quantum nanoparticles are quantum dots,
16 quantum wires, quantum wells, or quantum rods.
- 17 15. The method of claim 13 wherein the group IB element is copper (Cu), the group IIIA
18 element is indium and optionally includes gallium) and the group VIA element is
19 selenium (Se) or sulfur (S) and a stoichiometric ratio of the Cu, In and Se or S in the
20 liquid is approximately $\text{CuIn}_{1-x}\text{Ga}_x(\text{S or Se})_2$, where x is between 0 and 1.

- 1 16. The method of claim 13 wherein forming non-oxide quantum nanoparticles includes a
2 reaction of the type:
3 $\text{CuCl} + \text{InCl}_3 (+\text{GaI}_3) + \text{TOPSe(S)} + \text{TOPO} \rightarrow \text{Cu(Ga, In)Se(S)}_2$.
- 1 17. The method of claim 13 wherein forming a mixture of non-oxide quantum nanoparticles
2 includes performing a reaction of the type:
3 $\text{CuCl (or CuI or CuCl}_2) + \text{InCl}_3 (\text{or InI}_3 \text{ or GaI}_3) + \text{Na}_2\text{Se} + \text{ligand/capping agent} \rightarrow$
4 Cu(Ga,In)Se_2 .
- 1 18. The method of claim 13 wherein the ligand/capping agent is selected from the group of
2 phosphines, amines, alcohols, thiols, ethers, water and glycols, trioctylphosphine oxide,
3 trioctylphosphine, triphenylphosphine, pyridine, methanol, ethanol, propanol, butanol,
4 ethane thiol, tetrahydrofuran, ethers, ammonia, methyl amine, ethylamine,
5 ethylenediamine, and acetonitrile.
- 1 19. The method of claim 13 wherein forming a mixture of non-oxide quantum nanoparticles
2 includes reacting a single-source precursor to form particles of IB-IIIA-VIA material.
- 1 20. The method of claim 19 wherein the single-source precursor is $(\text{PPh}_3)_2\text{CuIn(SET)}_4$ or
2 $(\text{PPh}_3)_2\text{CuIn(SePh)}_4$.
- 1 21. The method of claim 13 wherein forming a mixture of non-oxide quantum nanoparticles
2 includes spray co-precipitation of two or more reactants.
- 1 22. The method of claim 21 wherein one of the two or more reactants is selected from the
2 group of metal halides, metal acetates, metal sulfates, metal nitrates, metal alcoholates,
3 metal carbonates, metal phenolates, metal hydroxides, and organometallics.
- 1 23. The method of claim 22 wherein the two or more reactants include one or more reactants
2 of the type X/Hal, where X is Cu or In and Hal is chlorine (Cl) or iodine (I).
- 1 24. The method of claim 23 wherein the two or more reactants further include thiourea or
2 selenourea.
- 1 25. The method of claim 13 wherein forming a mixture of non-oxide quantum nanoparticles
2 includes performing a reaction of the type:
3 $(\text{IB})(\text{Et}_2\text{CN(VIA)}_2)_2 + \text{TOPO} \rightarrow \text{IB-VIA}$

- 1 26. The method of claim 25 wherein IB is Cu and VIA is Se or S.
- 1 27. The method of claim 13 wherein forming a mixture of non-oxide quantum nanoparticles
 - 2 includes performing a reaction of the type:
 - 3 $(\text{IB})(\text{Hal}) + \text{Na}_2(\text{VIA}) + \text{ligand/capping agent} \rightarrow \text{IB-VIA} + 2\text{Na}(\text{Hal})$
- 1 28. The method of claim 27 wherein the ligand/capping agent is selected from the group of
 - 2 trioctylphosphine oxide, trioctylphosphine, triphenylphosphine, pyridine, alcohols
 - 3 (methanol, ethanol, propanol, butanol), ethane thiol, tetrahydrofuran, ethers, ammonia,
 - 4 amines (methyl amine, ethylamine, ethylenediamine) and acetonitrile.
- 1 29. The method of claim 27 wherein the reaction is of the type:
 - 2 $\text{CuCl}_2 + \text{Na}_2\text{Se} + \text{Pyridine} \rightarrow \text{CuSe} + 2\text{NaI}$.
- 1 30. The method of claim 13 wherein forming a mixture of non-oxide quantum nanoparticles
 - 2 includes performing a reaction of the type:
 - 3 $(\text{IB})(\text{Hal}) + (\text{IIIA})(\text{Hal}) + \text{Na}_2(\text{VIA}) + \text{Ligand/Capping Agent} \rightarrow \text{IB-IIIA-VIA}$
- 1 31. The method of claim 30 wherein the reaction is of the type:
 - 2 $2\text{InI}_3 + 3\text{Na}_2\text{Se} \rightarrow \text{In}_2\text{Se}_3 + 6\text{NaI}$.
- 1 32. The method of claim 13 wherein forming a mixture of non-oxide quantum nanoparticles
 - 2 includes sonochemical synthesis of nanoparticles particles containing Se with Cu or In or
 - 3 Ga.
- 1 33. The method of claim 13 wherein forming non-oxide quantum nanoparticles includes
 - 2 preparing metal nanoparticles containing elements of groups IB, IIIA, VIA or a IB-IIIA-
 - 3 VIA alloy, by laser ablation, nucleation from vapor, exploding wires by electrical current
 - 4 surge, thermal decomposition of organometallic compounds, sonolysis, pulse radiolysis,
 - 5 electrochemical reduction or chemical reduction.
- 6 34. The method of claim 13 wherein the liquid is formed by mixture with water.
- 7 35. The method of claim 13 wherein the liquid is formed by mixture with organic solvent.
- 8 36. The method of claim 13, further comprising adding a capping agent to the non-oxide
 - 9 quantum nanoparticles.

- 10 37. The method of claim 13, further comprising adding a binder to the non-oxide quantum
11 nanoparticles.
- 1 38. The method of claim 13, further comprising adding a fluxing agent to the non-oxide
2 quantum nanoparticles.
- 1 39. The method of claim 13, further comprising adding one or more surfactants, polymers,
2 dispersants, binders, modifiers, detergents or additives to the non-oxide quantum
3 nanoparticles.
- 4 40. A method for fabricating a liquid containing intermixed elements of groups IB and IIIA
5 and optionally VIA, comprising the steps of:
6 forming nanoparticles from group IB; and
7 intermixing the nanoparticles from group IB with elements from group IIIA, wherein the
8 elements from group IIIA are in molten form, wherein the nanoparticles from group IB
9 comprise particles in a desired particle size range of between about 0.1 nm and about 500
10 nm in diameter, wherein a majority of the mass of the nanoparticles range in size from no
11 more than about 40% above or below an average particle size, or, if the average particle
12 size is less than about 5 nanometers, from no more than about 2 nanometers above or
13 below the average particle size; and
14 mixing the nanoparticles with the molten elements to form a liquid that serves as an ink.
- 15 41. The method of claim 40 wherein the group IB element is copper (Cu), the group IIIA
16 element is indium and optionally includes gallium) and the group VIA element is
17 selenium (Se) or sulfur (S) and a stoichiometric ratio of the Cu, In and Se or S in the
18 liquid is approximately $\text{CuIn}_{1-x}\text{Ga}_x(\text{S or Se})_2$, where x is between 0 and 1.
- 1 42. The method of claim 41 wherein a majority of the group IB nanoparticles range in size
2 from no more than about 40% above or below an average nanoparticle size, or, if the
3 average nanoparticle size is less than about 5 nanometers, from no more than about 2
4 nanometers above or below the average nanoparticle size.
- 1 43. The method of claim 40, further comprising adjusting the temperature of the Cu-In-Ga
2 mixture until a solid forms and then grinding the solid to form nanoparticles.
- 1 44. The method of claims 1, 13, or 40 further comprising the step of capping the
2 nanoparticles with an organic material.

- 1 45. The method of claim 44 wherein the organic material is a small molecule with low
2 boiling point.
- 1 46. The method of claim 44 wherein the organic material is selected from the group of
2 trioctylphosphine oxide, trioctylphosphine, triphenylphosphine, pyridine, alcohols
3 (methanol, ethanol, propanol, butanol), ethane thiol, tetrahydrofuran, ethers, ammonia,
4 amines (methyl amine, ethylamine, ethylenediamine) and acetonitrile.
- 1 47. The method of claims 44 wherein the organic material is pyridine.
- 1 48. The method of claim 1, 13, or 40 wherein forming a mixture of non-oxide nanoparticles
2 includes selecting particles in the desired particle size range.
- 1 49. The method of claim 48, wherein selecting nanoparticles in the desired size range
2 includes adjusting one or more parameters of a reaction that forms the nanoparticles, size-
3 selective precipitation, or ultrafiltration.
- 1 50. The method of claims 1, 13 or 40 further comprising adding a water-compatible
2 dispersant to the liquid.
- 1 51. The method of claims 1, 13, or 40 wherein forming the non-oxide nanoparticles includes
2 preparing particles in a non-oxygen atmosphere.
- 1 52. A method for fabricating a liquid containing elements of groups IB, IIIA and optionally
2 VIA, comprising the steps of:
3 forming nanoparticles containing elements from groups IB, and IIIA and optionally VIA,
4 wherein the particles are in a desired particle size range of between about 0.1 nm and
5 about 500 nm in diameter, wherein a majority of the mass of the nanoparticles range in
6 size from no more than about 40% above or below an average particle size, or, if the
7 average particle size is less than about 5 nanometers, from no more than about 2
8 nanometers above or below the average particle size; and
9 mixing the nanoparticles to form a liquid that serves as an ink.
- 1 53. The method of claim 52 wherein the nanoparticles sizes are chosen to optimize their
2 melting points with respect to each other.
- 1 54. The method of claim 52 wherein the group IB element is copper (Cu), the group IIIA
2 element is indium and optionally includes gallium) and the group VIA element is

- 3 selenium (Se) or sulfur (S) and a stoichiometric ratio of the Cu, In and Se or S in the
4 liquid is approximately $\text{CuIn}_{1-x}\text{Ga}_x(\text{S or Se})_2$, where x is between 0 and 1.
- 1 55. The method of claim 52 wherein forming the metallic nanoparticles includes mixing one
2 or more liquid organometallic precursors of IB, IIIA and VIA elements.
- 1 56. The method of claim 52, further comprising burning organic components out of the ink
2 by heating.
- 1 57. The method of claim 52 wherein using one or more organic precursors includes forming a
2 sol-gel from the organometallics.
- 1 58. The method of claim 57, further comprising burning organic components out of the sol
2 gel by heating to produce a remnant mixture.
- 1 59. The method of claim 58, further comprising, after burning out the organic components,
2 exposing the remnant mixture to H_2 gas.
- 1 60. The method of claim 52 wherein mixing the nanoparticles to form the liquid includes
2 mixing a metal halide and a chelating agent.
- 1 61. A method for fabricating a photovoltaic cell active layer containing a IB-IIIA-VIA alloy,
2 comprising the steps of:
3 forming a liquid ink containing intermixed nanoparticles of elements from groups IB,
4 IIIA and optionally VIA, using the method of claim 1, 13, 40 or 52; spreading a film of
5 the liquid onto a substrate;
6 annealing the film to form the active layer; and
7 exposing the film to Se-containing vapor.
- 1 62. The method of claim 61, wherein the IB-IIIA-VIA alloy is an alloy of copper (Cu) with
2 indium (In) or Gallium (Ga) and selenium (Se) or sulfur (S) having a stoichiometric ratio
3 of the Cu, In and Se or S of approximately $\text{CuIn}_{1-x}\text{Ga}_x(\text{S or Se})_2$, wherein x is between 0
4 and 1.
- 1 63. The method of claim 61 wherein the substrate is a polymer or metallized polymer.
- 1 64. The method of claim 61, wherein annealing the film includes heating the film to a
2 temperature between about 200°C and about 600°C.

- 1 65. The method of claim 61, wherein the film is spread onto the substrate and/or annealed in
2 a roll-to-roll production system.
- 1 66. The method of claim 61, further comprising, winding the substrate into a coil and
2 exposing the coiled substrate to selenium vapor.
- 1 67. The method of claim 61 wherein annealing the substrate includes winding the substrate
2 into a coil and heating the coiled substrate.
- 1 68. The method of claim 61, further comprising winding the substrate into a coil and
2 depositing a layer of material on one or more surfaces of the coiled substrate.
- 1 69. The method of claim 61 wherein the layer of material includes a transparent conductive
2 oxide.
- 1 70. The method of claim 61 wherein forming the liquid, spreading the film of the liquid and
2 annealing the film does not include the use of H_2Se to selenize the particles, film or active
3 layer.
- 1 71. The method of claim 61 wherein forming the liquid, spreading the film of the liquid and
2 annealing the film does not include reduction of the particles, film or active layer with H_2 .
- 3 72. A photovoltaic cell, comprising:
4 a base electrode;
5 a top electrode; and
6 an active layer disposed between the base electrode and top electrode, the active layer
7 containing a IB-IIIA-VIA alloy, wherein the active layer is formed from a liquid ink
8 containing nanoparticles of elements from groups IB, IIIA and optionally VIA, using the
9 method of claim 1, 13, 50 or 52.
- 1 73. The cell of claim 72 wherein at least one of the base electrode and top electrode is
2 transparent.
- 1 74. The cell of claim 72 further comprising a layer of cadmium sulfide (CdS), zinc sulfide
2 (ZnS), or zinc selenide (ZnS) or some combination of two or more of these disposed
3 between the active layer and the top electrode.